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PART XXI

VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES

PART XXI. MASS SPECTROMETRIC STUDIES OF THE VAPORIZATION OF THE SULPHIDES OF CALCIUM, STRONTIUM AND BARIUM. THE DISSOCIATION ENERGY OF S_2 AND SO .

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FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Non-Graphitic." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio. Mr F. W. Vahldiek was the project engineer.

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ABSTRACT

CaS, SrS and BaS have been evaporated and the vapor analyzed by mass spectrometry. The following thermochemical data were obtained: $D_0^\circ(S_2)=97\pm5$; $D_0^\circ(CaS)=73.7\pm4.5$; $D_0^\circ(SrS)=74.1\pm4.5$; $D_0^\circ(BaS)=94.7\pm4.5$; $\Delta H(dim.BaS)=113.9\pm5$; $\Delta H_{298vap}(CaS)=148.0\pm5$; $\Delta H_{298vap}(SrS)=143.0\pm5$; $\Delta H_{298vap}(BaS)=122.5\pm5$; $D_0^\circ(CaO)=84.4\pm6$; $D_0^\circ(SrO)=92.2\pm6$; $D_0^\circ(BaO)=130.4\pm6$; $D_0^\circ(SO)=123.5$ kcal per mole.

This technical documentary report has been reviewed and is approved.

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INTRODUCTION.

In previous mass spectrometric studies[1,2] of the vaporization of the sulphides, selenides and tellurides of zinc, cadmium and mercury, no molecules formed of group II_b metal and group VI_b element were found although continuous spectra[3] had been ascribed to several of these molecules whose relative concentration in the saturated vapor is certainly lower than 10^{-4}. The present paper reports the mass spectrometric investigation of the saturated vapor above sulphides of the II_a elements Ca, Sr and Ba. The gaseous molecules CaS[4], SrS, BaS and Ba_2S_2 have been identified and their dissociation energies measured. Data on these molecules have hiterto been very scanty and again continuous spectra have been ascribed to these molecules[3].

Further it has been shown previously[1] that the study of the vaporization of compounds is a practical means of obtaining the vapors of its components in unsaturated and well defined concentrations and therefore of observing the dissociation of certain species at much lower temperatures than in the saturated vapor above the element.

The disagreement between second and third law values of $D_o^o(S_2)$ obtained from vapor density measurement of sulphur has been emphasized many years ago[5]. The spectrum of S_2 has been discussed in detail by Gaydon and by Herzberg[3] and more recent data have been reviewed by Brewer[6] and by Marsden[7]. In order to make a choice between "possible" spectroscopic values of the dissociation energy of S_2 it has been proposed[5] to relate this value to the dissociation energy of SO by an adequate thermochemical cycle. St.Pierre and Chipman[8] as well as Dewing and Richardson[9] have attempted to make the necessary thermodynamic measurements. Their results are partly contradictory and concern complicated systems which are not quite unambiguous by themselves.

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We have therefore studied the $S_2 \rightleftarrows 2S$ reaction in equilibrium with solid CaS, SrS and BaS and have obtained a value for the dissociation energy of S_2.

Some sulphide samples used in this work were strongly oxidised, in one case a mixture of sulphide and oxide was used: this permitted us to observe the gaseous oxides and the SO molecule in the same run as the sulphide and to obtain some information on the stability of these molecules. A more detailed study of oxides to be presented in a following paper[10] confirms these results and explains discrepancies of earlier measurements.

EXPERIMENTAL.

The sulphides were vaporized from molybdenum Knudsen cells with .5 to 1 mm diameter orifices and orifice sample surface area ratios smaller than 1/200. The main features of the crucible and source arrangements have been described[11]. The vaporization crucible with its radiation shields can be moved, on a silphon bellows attachment, with respect to a water-cooled copper collimating system which defines the entrance of the molecular beam into the ion source; this permits one to distinguish ions formed from species of the molecular beam and from species of residual gases or re-evaporated from radiation shields. Ions were formed by a 3 to 30 μA beam of 5 to 70 volt electrons and accelerated to 2000 eV. The ions were mass analyzed by a 20 cm radius of curvature, 60° sector, single focussing mass spectrometer. The ion current leaving the exit slit was accelerated to 4.500 eV., amplified by a nine stage Ag-Mg secondary electron multiplier and measured by a vibrating reed amplifier and pen recorder. Species were identified by mass, isotopic ratio and appearance potential.

A Leeds and Northrup disappearing filament optical pyrometer was used to measure the brightness temperature of a hole

drilled in the bottom of the molybdenum crucible. Emissivity measurements were made by comparison with a "black body" hole in graphite and corrections were made for window absorption. We believe that the accuracy is of about ±20° or ±1%.

The commercial samples of CaS and SrS (Hopkins and Williams), which were used, were highly oxidized and contained 58% SrS and 39% $SrSO_4$, 71% CaS and 28% $CaSO_4$, and some sulphite, hyposulphite, polysulphide and water. CaS and SrS samples, prepared according to Hartman and Ströhl[12], and BaS samples recrystallized from H_2S saturated aqueous solution contained only small amounts of oxides.

TREATMENT OF DATA.

1. Thermodynamic data have been obtained by using the third law method, i.e. the eqn.:

$$\Delta H_o^o + T\Delta\left((G_T^o - H_o^o)/T\right) = -RT\ln K = \Delta G_T^o \qquad (1)$$

ΔH_o^o is the enthalpy change at 0°K and $\Delta\left((G_T^o - H_o^o)/T\right)$ the change in free energy function (F.E.F.) accompanying the reaction.

The relation between the partial pressure of a given species and the resulting ion current is:

$$p_i S_i = I_i T$$

where T is the absolute temperature and S_i the sensitivity of the mass spectrometer for the isotope of abundance a_i of species i. Ratios of sensitivities are given by:

$$S_i/S_j = a_i\sigma_i\gamma_i/a_j\sigma_j\gamma_j \qquad (3)$$

here σ are the ionization cross sections and γ the multiplier efficiencies.

2. We have considered the equilibria:

$$2/3Me + 4/3S_2 \rightleftarrows 2/3(MeS) + 2S \qquad (i)$$

$$Me + S_2 \rightleftarrows MeS + S \qquad (ii)$$

$$Me + SO \rightleftarrows MeO + S \qquad (iii)$$

Me stands for Ca, Sr and Ba; square brackets () denote the

condensed phase. The corresponding equilibrium constants are pressure independent and are given by

$$K_{(i)}=\{I^2(S)/I^{2/3}(Me)I^{4/3}(S_2)\}\{(a\sigma\gamma)_{Me}{}^{2/3}(a\sigma\gamma)_{S_2}{}^{4/3}/(a\sigma\gamma)_S{}^2\}$$

$$K_{(ii)}=\{I(S)I(MeS)I(Me)I(S_2)\}\{(a\sigma\gamma)_{Me}(a\sigma\gamma)_{S_2}/(a\sigma\gamma)_{MeS}(a\sigma\gamma)_S\}$$

$$K_{(iii)}=\{I(S)I(MeO)/I(Me)I(SO)\}\{(a\sigma\gamma)_{Me}(a\sigma\gamma)_{SO}/(a\sigma\gamma)_{MeO}(a\sigma\gamma)_S\}$$

This procedure is equivalent to using equilibrium (5) as a pressure calibration instead of weight loss calibrations which appear to be unreliable and lead to irreproducible results due to uncontrolable side reactions. Weight loss calibrations are discussed in an appendix.

3. The mass dependence of the multiplier efficiency has been measured previously[13], the so-called molecular effect[14] was taken into account; the values obtained on this basis are given in table 1. Ionization cross sections for atoms were taken from Otvos and Stevenson[15]. For several homonuclear diatomic molecules and for dimers it has been found recently[16] that σ is approximately 1.5 times that of the monomers; similarly we have estimated for unsymmetric molecules $\sigma_{AB} = \sqrt{\sigma_A^2 + \sigma_B^2}$ (*). Thus we have obtained the log $a\sigma\gamma$ values of the last column of table 1; we believe that the error in using these values does not exceed 0.15 log units, especially as ratios are needed for the equilibria (i), (ii) and (iii).

4. For equilibrium (i):

$$\Delta G_T^o=D_o^o(S_2)-2/3\Delta H_o^o(5)+T\Delta FEF\{2(S)+2/3(MeS)-2/3(Me)-4/3(S_2)\} \quad (4)$$

ΔFEF is the difference of the free energy functions of the substances given in the brackets. $\Delta H_o^o(5)$ refers to the decomposition equilibrium eqn.(5)

$$(MeS) \rightleftarrows Me + 1/2S_2 \quad (5)$$

(*) This formula is used as a rule of thumb and no theoretical significance is attributed to it.

whose enthalpy change is obtained from the standard heat of formation of (MeS), and the heats of vaporization[17] of (Me) and (S). $\Delta H^{o}_{298,f}$(MeS) taken from the compilation of Freeman[18] and the values of FEF(MeS) given there, extrapolated to high temperatures are shown in table 2. The uncertainties of the heats of formation are given in table 2; for F.E.F. we estimate it to be ±2 e.u.; by eqn.(4) both errors are reduced to two thirds.

F.E.F. for the elements are taken from Stull and Sinke[17].

5. For equilibrium (ii)

$$\Delta G^{o}_{T}=D^{o}_{o}(S_2)-D^{o}_{o}(MeS) + T\Delta F.E.F.\{(S) + (MeS)-(S_2)-(Me)\} \qquad (6)$$

Here the best value of $D^{o}_{o}(S_2{}^{2}) = 99.4$ kcal mole^{-1} (see Discussion) is inserted and the free energy function of MeS are calculated as follows.

For CaS, SrS and BaS no data are available on interatomic distances (r_e) nor on vibration frequencies (ω_e). For the diatomic oxides and sulphides[3c,19] of C, Si, Ge, Sn, Pb, S and Mg the ratios r_e(Me-S)/r_e(Me-O) = 1.25 and ω_e(Me-O)/ω_e(Me-S)= 1.68 are fairly constant. We assumed that this relation holds also for oxides and sulphides of Ca, Sr and Ba and have used the molecular properties given in table 3. An error of 10% on r_e would results in an error of 0.3 e.u. for the rotational F.E.F., an error of 25% on ω_e results in an error of 0.5 e.u. for the vibrational F.E.F. The greatest uncertainty lies in the electronic contribution, since nothing is known about the electronic ground state and low lying excited states; we have taken Rln 3 with an uncertainty of ±2.2 e.u. This could be understood as the assumption of a $^{3}\Sigma$ ground state, or a $^{1}\Sigma$ ground state and low lying excited states. With the error limits quoted we believe to comprise all reasonable possibilities.

For Ba_2S_2 the empirical formula based on molecular mass, proposed by Kubaschewski and Evans[20] leads to $-(G_T^o - H_o^o)/T_{2000°} = 102$ e.u. assuming $C_p = 19.6$ cal/degree; for As_4[17] which has the same mass the value is however 94 e.u.; we have chosen the average 98±5 e.u.

6. For equilibrium (iii)

$$\Delta G_T^o = D_o^o(SO) - D_o^o(MeO) + T\Delta F.E.F.\{(S) + (MeO) - (SO) - (Me)\} \quad (7)$$

The dissociation limit of the SO molecule seems to be well established[21] as 123.5±0.25 kcal/mole^{-1}. The F.E.F. for SO has been taken from JANAF tables[22], for MeO from Brewer and Rosenblatt[19].

RESULTS.

On slight heating all samples first gave off smaller or larger amounts of CS_2, SO_2 and H_2S. This degassing was however small for experiments number 61.09; 61.10 (BaS) and for the samples prepared according to Hartmann and Ströhl[12] (experiments series 64); one set of experiments on SrS was discarded due to its high impurity content and because of inconsistent results.

Next the crucible was heated to the temperature range of 1750 to 2300°K in order to observe adequate ion intensities as shown for four typical runs in table 4. A number of points were taken in irregular sequence of temperature. As in all cases, except for BaS, the intensity of molecular ions is only a small fraction of atomic ions, it may be assumed that fragmentation can contribute only little to the latter. The ion intensities given for S^+ in table 4 and used for calculations have nevertheless been corrected, assuming 10% fragmentation of S_2 and MeS based on observations on S_2[1c,e] and other sulphides[23] at lower temperature.

to exist for the dissociation energy of SO where D(SO)=123.5 kcal or 97.0 are possible values. Measurements of the dissociation equilibrium presented here decide clearly in favour of the high values. This decision depends critically on the pressure calibrations. These have therefore been considered with geat care: equilibrium (i) appeared to be the most reliable pressure calibration in this case, and depends mainly on the thermodynamic data available for solid MeS . These are apparently sufficiently accurate (see Treatment of Data 4 and Results 1) to discard the low values of $D(S_2)$. Weight loss calibration using eqn.(1) and (2) and the Hertz-Knudsen equation were performed previously[4]; an effort was also made to take into account analytical data on the sulphides and side reactions. Finally this method appeared less reliable than the use of eqn.(4), (Treatment of Data 4 and appendix) even though the resulting $D(S_2)$ values, only 2-3 kcal lower, would also suffice to discard $D_o^o(S_2)$ = 83 and 75.5 kcal/mole..

b) Unfortunately the data of Berkowitz and Marquart[2] contain only apparently a value of $D(S_2)$ even though a figure is given[24], since pressure calibrations of these authors were unsuccessful.

c) The value $D_o^o(S_2)$ = 97±5 kcal found here is compatible either with an exact predissociation at 35,713 cm^{-1} = 4.43 e.v. = 102.1 kcal per mole, as proposed by Rosen, Duchesne et Désirant[26] or a repulsive curve causing the predissociation. Thermochemical cycles involving the heat of vaporization of GeS[29], SnS, PbS[23] and the dissociation energy of the gaseous molecules[30] seem to favour[24] a value $D_o^o(S_2)$ = 99.5±2.5 kcal per mole. Since Janaf tables[22] have tabulated values based on 99.4 kcal, we have accepted this value.

d) The equilibria studied by St.Pierre and Chipman[8] as well as by Dewing and Richardson[9] are in agreement with the present conclusions but due to the complex nature of the equilibria did not by themselves permit one to draw definite conclusions[24].

2. Few gaseous sulphides are as yet known[2,4,23,29-34]. The values proposed here for the dissociation energy of CaS and SrS are about 6 kcal lower than those given by Berkowitz and Marquart[2]; the difference is entirely due to a different choice of $D_o^o(S_2)$ and free energy functions. These authors have taken 1 for the electronic multiplicity, and use the value $D_o^o(S_2)$=101.4 kcal per mole, which is certainly an arbitrary choice. Earlier values we had given[4] of D_o^o(CaS) =69.3or71.0 and D_o^o(SrS)=73.9 kcal are in satisfactory agreement with our present calculations and were based on weight loss pressure calibrations.

It is interesting to compare as in table 6 and 7 some properties of oxides and sulphides which have quite parallel trends: the considerably larger increase in D(MeX) and decrease in ΔH^o_{vap}(MeX) from Sr to Ba than from Ca to Sr; D(MeS)-D(MeO) varies smoothly from -10, to -18 to -26 kcal and ΔH^o_{vap}(MeS)-ΔH^o_{vap}(MeO) from -11, to -3 to +20 kcal; sulphides of Ca and Sr are more volatile than oxides, whereas for Ba the reverse is the case. This has been observed already by Grattidge and John[34] by mass spectrometry, who do not however give data on the composition of the gas phase.

Special attention may be drawn to the magnitude α = ΔH(At.MeX)/D(MeX)[31] which, if $\alpha > 1$, indicates that the relative concentration in the saturated vapor increases with increasing temperature, or vice versa, if $\alpha < 1$. For both compounds of Ca and Sr α is considerably larger than 1: they are definitely

1. The dissociation energy of S_2.

For the reason discussed above equilibrium (i) was used for the calculation of third law values of $D_o^o(S_2)$ as given in tables 4 and 5. There is no trend of the values with temperature and the scatter of the results in each experiment and from one experiment to the other for CaS and SrS is satisfactorily small. The average for each substance is however somewhat different as shown in table 5 which summarizes all our experiments.

The values of tables 4 and 5 permit one to discard the "low values" $D_o^o(S_2)$ = 76 or 83 kcal. The rather lower value $D_o^o(S_2)$ found for SrS is readily explained by the larger uncertainty of the value of the standard heat of formation. In fact the error limits given in table 5 take into account (a) an error of 2-3 kcal due to the scatter of the ion intensity ratios, (b) the uncertainty in $2/3\Delta H^o_{298,f}(MeS)$: 1.7, 5.3 and 2.0 kcal for CaS, SrS and BaS respectively and finally (c) an estimated uncertainty of 0.15 for each $\sigma\gamma$ ratio. The conclusion of table 5 therefore is a value of $D_o^o(S_2)$ of 96 or 97 kcal with an error limit of 4 to 5 kcal.

Calculations of the equilibrium $S_2 \rightleftarrows 2S$ as $\log I^2(S)T/I(S_2)$ as a function of 1/T yield second law values of $D_o^o(S_2)$=110 kcal per mole indicating that the parameters used in the third law calculation lead to a somewhat low value. However the error in second law calculations due alone to temperature uncertainties may be as high as ±10 kcal and therefore does not permit one to draw further conclusions. **However, there are reasons to be discussed** below[24] to accept the value of $D_o^o(S_2)$ = 99.4±2.5 kcal; which was used for further calculations.

Taking into account this latter value, the heats of formation of the three sulphides given in the literature and

the combined error of our measurements and of literature data, a new set of $\Delta H^{o}_{298,f}(MeS)$ values is obtained (see footnote table 2).

2. The dissociation energy and heat of vaporization of CaS, SrS, BaS and Ba_2S_2.

Equilibrium (ii) was used, inserting the thermodynamic data discussed above and the value $D^{o}_{o}(S_2) = 99.4$ kcal. The results are given in table 4 and 6; again the results are extremely selfconsistent, the main uncertainty being the electronic contribution to the free energy function.

The heats of vaporization given in table 6 were obtained from the selected values given in table 2 for reaction (5), $D^{o}_{o}(S_2) = 99.4$ and $D^{o}_{o}(MeS)$.

Finally the equilibrium

$$(BaS) + BaS \rightleftarrows Ba_2S_2$$

yields the dimerization energy of BaS and the heat of vaporization of Ba_2S_2 given in tables 4 and 6.

3. The dissociation energy of CaO, SrO, BaO and SO.

In a few cases (see table 4) MeO and SO were observed simultaneously permitting us to use equilibrium (iii) to calculate D(SO) - D(MeO); taking $D^{o}_{o}(SO) = 123.5$ kcal per mole[21] the values given in tables 4 and 6 are obtained. Due to the small number of points **and to the low intensities (the error may be of** 2 units given in table 4), the error limits (see table 6) have been increased.

DISCUSSION.

1.a) Three values of the dissociation energy of S_2 viz. ≈ 75.7 ≈ 83, $\approx$ **102.1** kcal are compatible with the predissociation limit observed[26,3b] as had been pointed out many years ago[5,27]. Purely spectroscopic arguments do not permit one to make a choice among these values[24]. A similar situation seems

high temperature molecules; this seems doubtful for the oxide and sulphide of Ba and for the dimers. If, as may be considered probable, the α values for the dimers of Ca and Sr compounds are not very different of those of the Ba compounds, it would be very difficult to observe them with present experimental possibilities, even though the dimerization energy would not differ much from that of the Ba compounds.

3. The results we have obtained for the oxides are, as pointed out above, subject to considerable experimental error. Nevertheless they are of interest for several reasons.

The magnitude actually measured was D(SO)-D(MeO). Since D(SO) results from an exact predissociation[35] two values of D_0^0(SO) could at least be considered: 123.5 kcal[21] or 97.0 kcal. The latter would however lead to D(MeO) values completely in contradiction with best available data[10,25]. This way of discarding the lower value may be more reliable than any one proposed previously[7,36]. As pointed out by Norrish and Oldershaw[21] there is a slight possibility that the numbering of the vibrational levels of the ground state of SO is not yet accurate and that it may be necessary to increase v" by one or two, increasing therefore D_0^0(SO) by nearly 3 or 6 kcal. Whereas a 3 kcal increase could be compatible with our experimental uncertainty, 6 kcal may be discarded.

Our data have drawn our attention to the apparent irregularity of literature data on dissociation energies of group IIa oxides. The difficulties arrising in these measuremants especially for SrO[25] have been investigated now by Drowart and coworkers[10] and will be discussed by these authors.

TABLE 1. Relative sensitivities.

Species	γ	σ	$\log a_{\sigma\gamma}^{(*)}$
S^{32}	1	12.8	1.09
Ca^{40}	0.97	42.1	1.60
Sr^{88}	0.77	64.3	1.61
Ba^{138}	0.55	78.1	1.49
S_2^{64}	0.96	19.2	1.22
SO^{48}	1.05	13.5	1.13
CaO^{56}	1.01	45	1.64
CaS^{72}	0.92	50	1.63
SrO^{104}	0.76	65	1.61
SrS^{120}	0.70	75	1.62
BaO^{154}	0.58	80	1.52
BaS^{170}	0.52	85	1.48
$Ba_2S_2^{340}$	0.42	100	1.30

TABLE 2. Thermodynamic properties of solid CaS, SrS and BaS.

$-\Delta H^{o}_{298f}(MeS)^{(*)}$ kcal mole^{-1}		$-(G^{o}_{T} - H^{o}_{298})/T^{(**)}$ e.u.			
		1500	1800	2100	2400°K
CaS	114.5±2.0	23.0	25.0	26.8	28.6
SrS	108.1±8.0	26.3	28.4	30.4	32.3
BaS	108.0±3.0	29.4	31.9	34.3	36.6

(*) If the value $D^{o}_{o}(S_2)$ = 99.4±2.5 kcal is accepted (see Results and Discussion) our results and the above thermochemical data yield as best values:

	$-\Delta H^{o}_{298f}(MeS)$
CaS	114.8±1.5
SrS	113.1±1.5
BaS	110.4±1.5

which are in better agreement with v. Wartenberg's choice (Z.anorg.Ch., 1943, 252, 142) of best values 114, 113, 111 kcal than with Freeman's[18].

The heat of reaction for $(MeS) \rightleftarrows Me + 1/2S_2$ (eqn.5) is then:

	CaS	SrS	BaS
$\Delta H^{o}_{o}(5)$ =	172.0	167.4	167.5

The low temperature heat capacity curves of King and Weller (U.S. Bureau of Mines, R.I. 5590, 1960) have been integrated to obtain $\Delta H^{o}_{o}(5)$.

(**) Fusion, which occurs at about 2300°K has not been taken into account as our experimental data lie below the melting point.

TABLE 3. Molecular properties of gaseous sulphides of Ca, Sr and Ba.

	r_e (Å)	ω_e (cm^{-1})	$-(G_T^o-H_o^o)/T$ (e.u.)		
			1700°	2000°	2300°K
CaS	2.27	435	64.4	65.8	67.0
SrS	2.42	388	66.9	68.3	69.6
BaS	2.42	397	67.8	69.2	70.5

TABLE 4

Exp.no & Substances	T°K	Ion current in arbitrary units at mass number						$D_o^o(S_2)$	$D_o^o(MeS)$	$D_o^o(MeO)$
		32 S[a]	40 Ca	48 SO	56 CaO	64 S_2	72 CaS			
61.05 CaS oxidized	2072	640	1200	-	-	192	18	96.5	74.0	-
	2073	817	1440	78	-	225	(16)	95.9	73.1	-
	2085	879	1650	90	-	216	21	95.3	74.0	-
	2121	1491	2130	129	-	390	30	94.7	73.7	-
	2180	3114	5300	380	8	860	93	95.2	73.7	80.3
	2209	3892	6800	480	-	1080	114	95.4	73.2	-
	2319	12050	24000	1590	21	2490	460	92.0	73.8	83.4
	2386[c]	121	12300	105	330	-	-	-	-	89.4
							average	95.0	73.6	84.4
64.03	1849	84	234	-	-	32	-	99.6	-	-
	1861	108	320	-	-	39	-	99.4	-	-
	1962	360	880	-	-	129	-	98.5	-	-
	1962	390	1050	-	-	141	-	99.7	-	-
	2047	1320	3800	-	-	470	-	98.7	-	-
	2058	1110	3300	36	-	410	35	98.9	-	-
	2155	4000	10500	108	-	1110	117	96.7	-	-
							average	98.8		

TABLE 4. Continued

		32 S[a]	48 SO	64 S_2	88 Sr	104 SrO	120 SrS			
64.05 mixture of SrS + SrO	1745	15	11	10	159	10	-	100.5	-	-
	1857	48	14	5	730	-	-	92.4	-	-
	1885	69	22	10	900	-	-	93.6	-	-
	1892	102	40	23	550	-	-	93.6	-	-
	1931	132	43	23	1770	5	-	92.5	-	90.3
	1981	102	40	23	550	-	-	93.3	-	-
	1996	430	140	49	1665	-	-	92.5	-	-
	2010	300	84	50	3000	20	30	93.4	75.0	93.0
	2087	1260	440	300	4900	60	57	92.4	73.2	93.3
	2101	1590	470	340	6000	57	72	91.8	73.6	92.7
	2170	3230	1080	632	9800	102	162	91.4	74.5	91.8
								93.4	74.1	92.2

TABLE 4. Continued

	T°K	Ion Intensities at Mass Number 32 S[a]	48 SO	64 S_2	138 Ba	154 BaO[b]	170 BaS	172 Ba_2S_2	$D_o^o(S_2)$	$D_o^o(MeS)$	$D_o^o(MeO)$	$\Delta H_o^o(dim)BaS$
61.09/10	1846	168	-	27	144	288	90	-	91.7	93.4	-	-
BaS	1923	220	-	36	470	-	570	-	94.9	95.6	-	-
	1934	350	7	36	330	252	360	-	90.3	96.9	130.9	
	1964	634	-	81	900	69	1080	-	92.5	96.4	-	-
	1973	323	-	69	1080	(16)	1200	11	96.4	94.1	-	114.4
	2019	420	7	84	1050	630	1140	-	96.2	94.1	131.1	-
	2041	890	-	159	2460	-	2640	29	95.9	94.5	-	115.0
	2069	826	4	165	1980	216	2370	-	96.1	94.4	129.3	-
	2105	1260	-	280	3200	-	3100	-	96.8	93.0	-	-
	2120	2320	-	400	4700	-	5400	35	94.8	94.7	-	112.4
									94.6	94.7	130.4	113.9

(a) The ion intensity of S has been corrected for approximately 10% fragmentation of S_2 and sulphides.

(b) In the vaporization of the BaS sample in early stages BaO and SO were observed, later these peaks disappeared; this explains the irregular trends in these columns written in order of temperature not in chronological order.

(c) This point shows a typical situation where most of CaS has evaporated and the sample seems to contain mainly CaO.

TABLE 5. Dissociation Energy of S_2.

	Exp.no	Number of points	$D_o^o(S_2)$ 3d law	Temperatures °K
CaS	61.02	14	96.9*	1900-2265
	61.05	7	95.0	2072-2319
	64.02	9	98.6	1764-2034
	64.02b	3	98.2	1765-1906
	64.03	7	98.8	1849-2155
			97.4±4.5**	
SrS	64.04	7	93.7	1907-2171
	64.05	11	93.4	1745-2170
			93.5±7**	
BaS	61.09/10	10	94.6±5.5**	1846-2120

* This experiment has been published earlier[4] using the weight loss calibration, which yielded $D_o^o(S_2)$ = 94.8 kcal/mole^{-1}.

** If von Wartenberg's ΔH_f(MeS) had been taken the experiments with CaS, SrS and BaS would yield respectively $D_o^o(S_2)$=97.2; 96.5; 96.6.

TABLE 6. Dissociation Energies and Heats of Vaporization of Sulphides and of Oxides of Ca, Sr and Ba.

	Exp.no	Number of points	D_o^o(MeS)	ΔH_o^o(vap.MeS)	Temperatures
CaS	61.02	9	74.3	147.4	2028-2265
	61.05	7	73.6	148.1	2072-2319
	64.02/3	7	72.9	148.8	1878-2155
		average	73.7±4.5	148.0	
SrS	64.04	6	74.1	143.0	1969-2171
	64.05	4_a	74.1	143.0	2010-2070
		average	74.1±4.5	143.0	
BaS	61.09	4	94.6	122.0	1846-2120
	61.10	10	94.7	122.5	
		average	94.7±4.5	122.5	
			ΔH_o^o(dim)		
Ba_2S_2	61.10	3	113.9±5	131.1±5	1973-2120
			D_o^o(MeO)	ΔH_o^o(vap.MeO)	
CaO	61.05	3	84.4±6	169.0	2180-2386
			(a)(82.6)		
SrO	64.05	5	92.2±6	146.1	1931-2170
			(a)(92.4),(b)(83.6)		
BaO	61.10	3	130.4±6	102.9	1934-2069
			(b)(130.2)		
Ba_2O_2	-	-	(a)(89±11)	(116)	-

In brackets the values of (a) Drowart et al.[10] and (b) Ingham et al.[25] or calculated therefrom. ΔH_o^o(vap.MeO) values are calculated with the average values of these authors and those obtained in this work.

TABLE 7. Properties of Gaseous Sulphides and Oxides of Ca, Sr and Ba.

	ΔH_o^o(f.gas) kcal per mole	ΔH_o^o(at.MeX)[b] kcal per at.gr	α[d]
CaO	17.7[a]	126.2	1.51
CaS	32.5	110.9	1.51
SrO	5.7[a]	119.2	1.29
SrS	30.0	108.6	1.47
BaO	-29.7[a]	116.6	0.89
BaS	12.0	108.6	1.15
Ba_2O_2	148.6[a]	102.9[c]	1.16[e]
Ba_2S_2	89.9	122.5[c]	1.08[e]

(a) The calculation is based as in table 6 on D_o^o(CaO)= 83.5 and D_o^o(SrO)=92.3 from Drowart, Exsteen and Verhaegen[10], D_o^o(BaO) = 130.3 and ΔH_o^o(dim.BaO) = 89.kcal[25].

(b) ΔH_o^o(at.MeX) corresponds[29] to the reaction

$$1/2(MeX) = 1/2Me + 1/2X$$

(c) Heat of vaporization of BaS and BaO.

(d) $\alpha = \Delta H_o^o(at.MeX)/D_o^o(MeX)$

(e) $\Delta H_o^o(vap.MeX)/\Delta H_o^o(dim.MeX)$.

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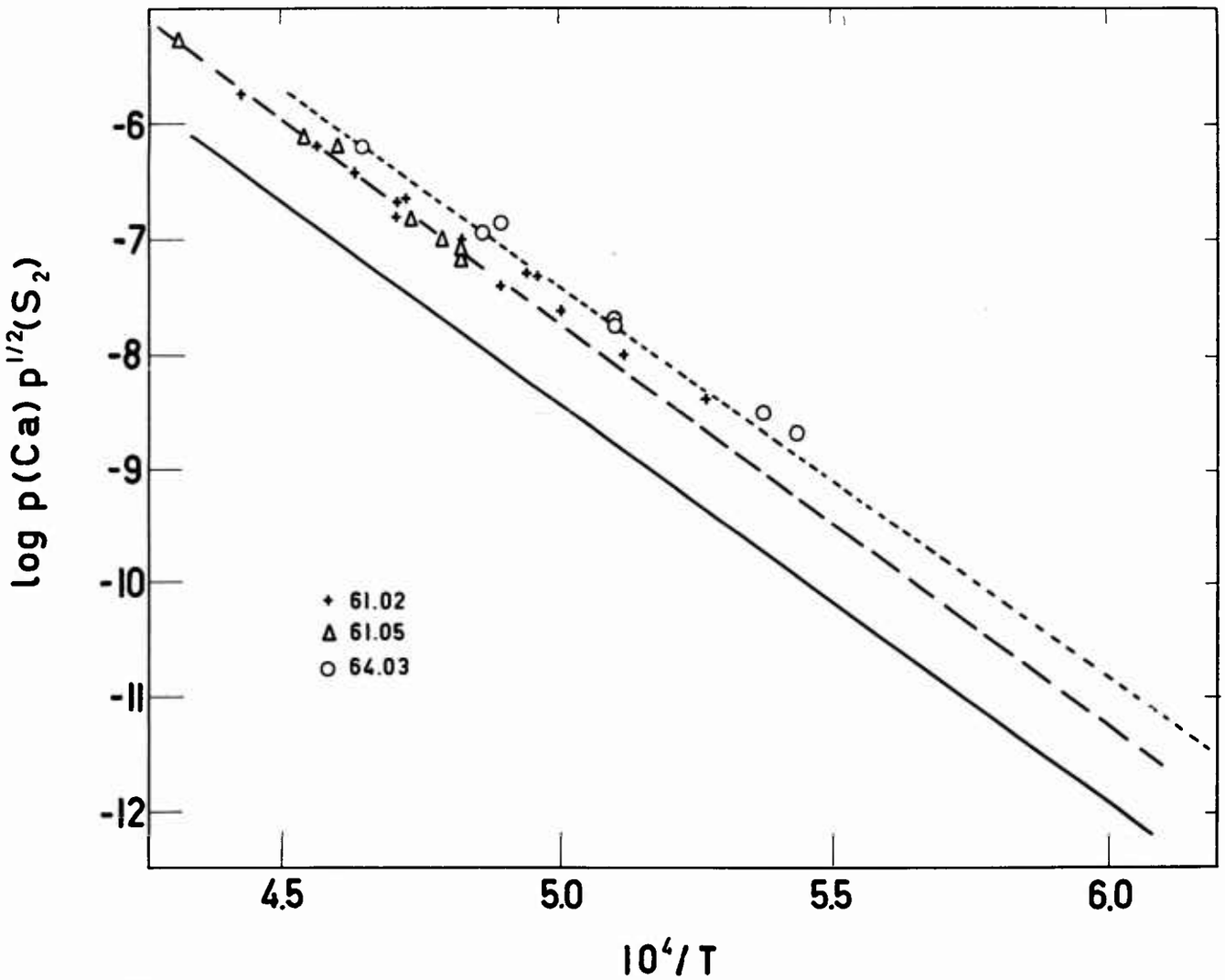

Fig. 1

APPENDIX

Weight loss sensitivity calibrations.

In the case of vaporization of a pure substance weight loss sensitivity calibrations are straightforward and based on the use of the Hertz-Knudsen effusion equation (eqn.1) and the definition of the sensitivity factor (eqn.2).

$$Z_i m_i = G_i = p_i (M_i / 2\pi RT)^{1/2} s \Delta t \qquad (1)$$

$$p_i S_i = I_i T \qquad (2)$$

here Z_i is the number of molecules of species i effusing through area s in time Δt; m_i the mass of one molecule and G_i the effusing mass; p_i is the pressure in dyne cm^{-2}; M_i the molecular weight in a.m.u.; R the gas constant in erg per degree and mole and T the absolute temperature; I_i is the observed ion current; S_i is the sensitivity factor in ion currentx°K per pressure units.

1. For a pure sulfide MeS which evaporates congruently according to

$$(MeS) \rightleftarrows Me + (1 - \alpha)S + \frac{\alpha}{2} S_2 \qquad (3)$$

and

$$(MeS) \rightleftarrows MeS \qquad (4)$$

the stoichiometry of vaporization is described by

$$G_{Me} = m_{Me} (Z(Me) + Z(MeS)) = GM(Me)/M(MeS) \qquad (5)$$

and

$$G_S = m_S (Z(S) + 2Z(S_2) + Z(MeS)) = GM(S)/M(MeS) \qquad (6)$$

here G is the total weight and G_{Me} and G_S the weight of metal and sulfur respectively.

Inserting eqn.(5) or (6) in (1) and (2) yields respectively

$$S_{Me} = 44.33s\left(M(MeS)/GM^{1/2}(Me)\right)\sum_{0}^{\Delta t} I(Me)T^{1/2}(1+\varepsilon_1)\Delta t$$
$$S_S = 44.33s\left(M(MeS)/GM^{1/2}(S)\right)\sum_{0}^{\Delta t} I(S)T^{1/2}(1+\varepsilon_2+\varepsilon_3)\Delta t \quad (8)$$

The numerical factor converts pressures to atmospheres; using eqn.(3) from Treatment of Data, ε_1, ε_2 and ε_3 may be written

$$\varepsilon_1=\left(M(Me)/M(MeS)\right)^{1/2}\left(I(MeS)/I(Me)\right)a\sigma\gamma(MeS)/a\sigma\gamma(MeS) \quad (9)$$

$$\varepsilon_2=2\sqrt{2}\left(I(S_2)/I(S)\right)a\sigma\gamma(S)/a\sigma\gamma(S_2) \quad (10)$$

$$\varepsilon_3=\left(M(MeS)/M(S)\right)^{1/2}\left(I(MeS)/I(S)\right)a\sigma\gamma(S)/a\sigma\gamma(MeS) \quad (11)$$

As seen in table 4, in the present experiments the ion intensity ratios I(MeS)/I(Me), $I(S_2)/I(S)$ and I(MeS)/I(S) are always small, therefore the magnitudes ε could often be neglected or else considered as small correction factors; therefore the well-known uncertainty in ionization cross section ratios (σ) is not very relevant.

2. As mentioned above in "Results", several samples appeared to be impure as confirmed by chemical analysis (Table A.1). In order to perform an accurate sensitivity calibration the exact stoichiometry of all reactions that occur in the vaporization process should be known. Since this is not the case several assumptions were made and tested. Finally the set of equations (12) was adopted in which the vaporization process is decomposed in three stages, which for CaS seem to be actually consecutive steps, whereas for the other sulphides they occur simultaneously.

$$
\begin{array}{llll}
\text{I} & MeSO_4 + MeS \rightarrow 2MeO + SO_2 + 1/2S_2 & & (a) \\
\text{II} & MeS \rightarrow Me + S & & (b) \\
 & MeS \rightarrow Me + 1/2S_2 & & (c) \\
 & MeS + MeO \rightarrow 2Me + SO & & (d) \\
 & MeS \rightarrow MeS & & (e) \\
\text{III} & MeO \rightarrow MeO & & (f) \\
 & MeO \rightarrow Me + O & & (g) \\
 & MeO \rightarrow Me + 1/2O_2 & & (h)
\end{array}
\qquad (12)
$$

The total amount of sulfide vaporized as such or after conversion to oxide by reaction (12a) is given by

$$G(MeS)=m(MeS)\left(Z_{II}(Me)+1/2Z_{III}(Me)+Z(MeS)+1/2Z(MeO)\right) \qquad (13)$$

$$G(MeS)=m(MeS)\left(Z(S)+2Z(S_2)+1.5Z(SO)+Z(MeS)+1/2Z_{III}(Me)+1/2Z(MeO)\right) \qquad (14)$$

and the total amount of sulphate by

$$G(MeSO_4) = m(MeSO_4)\left(1/2Z_{III}(Me)+1/2Z(SO)+1/2Z(MeO)\right) \qquad (15)$$

As seen in table 4, the ion intensities of MeO^+ can be neglected. Inserting eqn.(1) and (2) in (13), (14) and (15) yields

$$G(MeS)=44.33(MeS)s\left(S(Me).M(Me)^{1/2}\right)^{-1}(1+\varepsilon_3)\sum_0^{\Delta t}\left\{I_{II}(Me)T^{1/2}\Delta t + 1/2I_{III}(Me)T^{1/2}\Delta t\right\} \qquad (16)$$

$$=44.33M(MeS)s\left(S(S).M(S)^{1/2}\right)^{-1}(1+\varepsilon_2+\varepsilon_3+\varepsilon_4)\sum_0^{\Delta t}\left\{I(S)T^{1/2}\Delta t + 1/2\left(S(Me)M(Me)^{1/2}\right)^{-1}I_{III}(Me)T^{1/2}\Delta t\right. \qquad (17)$$

and

$$G(MeSO_4)=(1/2)44.33M(MeSO_4)s\left(S(Me).M(Me)^{1/2}\right)^{-1}(1+\varepsilon_5)I_{III}(Me)T^{1/2}\Delta t \qquad (18)$$

In eqn.(5-10), Z_{II} and $Z_{III}(Me)$ are the numbers of atoms Me vaporizing in reaction II and III respectively and $I_{II}(Me)$ and $I_{III}(Me)$ the corresponding ion intensities. The correction

terms are

$$\varepsilon_4 = \sqrt{1/6}\,[I(SO)/I(S)]\,a\sigma\gamma(S)/a\sigma\gamma(SO) \qquad (19)$$

$$\varepsilon_5 = 1/2\,I(SO)/I_{III}(Me)\,(a\sigma\gamma(Me)/a\sigma\gamma(SO)\,[M(Me)/M(SO)]^{1/2} \qquad (20)$$

Here as well as in eqn.(9-11) I stands for $I(\ )T^{1/2}\Delta t$.

Equations (16) and (18) permit one in the case of CaS to check the analysis; using the data of table A.2 one finds 31.6 and 25.8% $CaSO_4$, 68.4 and 74.2 CaS: the average with a deviation of 10%, corresponds to the result of the analysis performed by conventional methods (table A.1). We have not investigated whether the scatter is due to the method or to inhomogeneities of the samples as the uncertainty results only in an error of less than 5% in sensitivity factors. On the other hand for SrS from the analytical data I_{II} and I_{III} are calculated from eqn.(16) and (18) and S(Sr) obtained from (16) and (17). The necessary experimental data are summarized in table A.2 and the results are given in table A.3.

The results of table A.3 seem to be reasonably consistent and the variation of sensitivity over a large span of time not to considerable[(*)]. However the ratio of sensitivities S(Me)/S(S) are not in agreement with the estimated $a\sigma\gamma$ ratios (table 1) and especially the trend of their ratio from Ca to Ba is in contradiction with expectations.

Further these sensitivity factors were used to calculate equilibrium (5) (Treatment of Data). Fig.1 shows the results for CaS, for which most extensive data are available and their comparison with the equilibrium pressure calculated from thermodynamic data[18]. There is a noticeable disagreement. Also if $D_o^o(S_2)$ is calculated from these calibrations a considerable

[(*)] Exp.Nos.64 have been performed over a year after set 61.

scatter of the results would be observed for each sulfide.

The conclusion from all these results is that beside the impurity effects and the reaction (12) other side reactions perturb these calibrations; actually H_2S and CS_2 were observed; it has also been observed by Drowart and coworkers, after these experiments had been concluded, that alcaline earth oxides react with W and Mo to give volatile compounds. All these effects, whose importance is difficult to estimate, should be negligible if equilibrium (5) is used as a sensitivity calibration and the accuracy finally depends mainly on the accuracy of the thermodynamic data in this equilibrium. This was the procedure finally adopted.

TABLE A.1.

	Ca sulfide sample	Sr sulfide sample
MeS	69.41	56.06
$MeSO_4$	27.85	37.10
$MeSO_3$	0.34	-
MeS_2O_3	0.64	4.85
Polysulfide S	-	0.66
$Me(OH)_2$	0.63	0.21
H_2O	0.50	1.00
	99.37	99.88

(Thanks are due to Prof. Leroy of Institut Meurice-Chimie, Brussels, for performing these analysis).

TABLE A.2.

Integrated Ion Intensities

$I(\quad)T^{1/2}dt$ in scale division $(°K)^{1/2}$ sec x 10^{-7}

(1)	(2) Exp.n°	(3) Me^+(II)	(4) Me^+(III)	(5) S^+	(6) S_2^+	(7) SO^+	(8) MeS^+	(9) MO^+	(10) d	(11) $G^{(tot)}$
CaS	61.02	156	102	84	7.8	19.2	1.8	-	0.5	62.0
	61.05	825.6	374.4	426.6	7.8	18.2	1.8	-	0.5	120.25
	64.03	165.6	-	61.5	-	19.8	0.6	-	1.05	33.57
SrS	64.04	189.6	-	72.6	-	18.0	2.4	-	1.05	31.37
BaS	61.10	110.4	-	61.62	-	8.4	11.58	1.8	0.5	73.75

The headings of columns 3-9 refer to the ionic species: Me^+(II) and Me^+(III) corresponding to reaction II and III, eqn.(12); for SrS the observed ion current has been subdivided into Me^+(II) and Me^+(III) eqn.(16) and (18); Col.10 gives the orifice diameter of the effusion cell in mm. Col. 11 gives the weight of sample evaporated in mgr.

TABLE A.3. Sensitivity Factors

	Exp. no	log S(Me)	log S(S)
	61.02	10.67	10.36
CaS	61.05	11.05	10.72
	64.03	11.33	10.86
SrS	64.04	11.46	11.20
BaS	61.04	10.27	9.71